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CORRELATION EFFECTS AND MOLECULAR TUMBLING  
IN NMR STUDIES OF SOLID  $\beta$ - $(\text{CH}_3)_4\text{Si}$   
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Correlation Effects and Molecular Tumbling in NMR Studies of  
Solid  $\beta-(CH_3)_4Si$

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Abstract

The  $\beta$  phase of high purity samples (99.9% min) of tetramethylsilane (TMS),  $(CH_3)_4Si$ , was investigated between 77°K and its melting point (174°K) employing static and rotating frame proton spin-lattice relaxation ( $T_1$  and  $T_{1\rho}$ , respectively) measurements. Minima in the  $T_1$  curve near 90°K and in  $T_{1\rho}$  at 171°K correspond to methyl group reorientation and overall molecular tumbling, respectively. Activation energies and inverse frequency factors for both motions are derived and discussed. Deviations from exponential behavior in the longitudinal relaxation were noted below 140°K and are inferred to be due to a correlation in the relative motion of the protons within each methyl group. The exponentiality of the spin-lattice relaxation above ~140°K is associated with the onset of overall molecular tumbling motions. It is suggested that the presence of exponential proton magnetization decays in solids containing methyl groups may sometimes serve as an indication for the presence of reorientations of the molecular frame to which the methyl groups are attached. The possibility that the existence of exponential and nonexponential decays may be used by itself to gain information on interactions and motions in solids, has to be further investigated.

## INTRODUCTION

NMR investigations have been carried out on solid  $(CH_3)_4Z$  compounds, where  $Z = C, Si, Ge, Sn$  and  $Pb$ .<sup>1-3</sup> The presence of molecular reorientations in these substances was determined from the temperature dependence of the line width and second moment between 77°K and the respective melting points.<sup>1,3</sup> For most of these compounds the spin-lattice relaxation time ( $T_1$ ) vs. temperature behavior was also obtained,<sup>2,3</sup> however a very large scatter in the measured  $T_1$  points is evident<sup>3</sup> for  $(CH_3)_4Ge$ ,  $(CH_3)_4Sn$  and  $(CH_3)_4Pb$ . In the case of neopentane,  $(CH_3)_4C$ , the rotating frame spin-lattice relaxation time ( $T_{1\rho}$ ) was recently reported.<sup>4</sup>

From thermal studies<sup>5</sup> it was concluded that tetramethylsilane (TMS) crystallizes in two forms, a low temperature stable  $\beta$  phase and a high temperature metastable  $\alpha$  modification obtainable only in a temperature interval of 8-10°.<sup>3,5</sup> To the best of our knowledge no NMR relaxation studies have been reported on TMS. In the present paper static and rotating frame spin-lattice relaxation data are reported for the  $\beta$  phase of TMS, in which methyl group rotation as well as overall molecular tumbling take place.<sup>3</sup> The combined  $T_1$  and  $T_{1\rho}$  measurements enable us to study these motions in more detail and to get reliable activation energies, inverse frequency factors etc. for each of these reorientations. Deviations from exponential behavior observed for the static frame spin-lattice relaxation are demonstrated and discussed in our study.

## EXPERIMENTAL

High purity NMR grade (99.9% min) tetramethylsilane, provided by Aldrich Chemical Company, Incorporated, Milwaukee, Wisconsin, was used in

our experiments. Our samples were degassed by repeated freeze-pump-thaw cycles and then sealed under vacuum in pyrex tubes.

The static and rotating frame proton spin-lattice relaxation times for TMS were measured at a frequency of 25.3 MHz with the apparatus and methods described previously.<sup>6</sup> The measurements ranged from liquid nitrogen temperature ( $77^{\circ}\text{K}$ ) to the melting point ( $174^{\circ}\text{K}$ ). The variation in the length of the free induction decay following a  $90^{\circ}$  pulse was observed qualitatively, so that noticeable changes in the spin-spin relaxation time ( $T_2$ ) could be distinguished in the temperature region in question. The rf magnetic field amplitude  $H_1$ , utilized in our  $T_{1\rho}$  experiment was 3.3 gauss.

The  $\beta$  phase of TMS was obtained by cooling our samples below  $163^{\circ}\text{K}$ , that is below the lowest temperature at which the  $\alpha$  phase exists. Once the  $\beta$  phase was obtained, the temperatures of measurement were attained by cooling the sample down to  $77^{\circ}\text{K}$  and then allowing it to warm.

## RESULTS AND DISCUSSION

### Spin-Spin Relaxation Time ( $T_2$ )

The proton spin-spin relaxation time in the  $\beta$  phase of TMS was found to be temperature independent between  $77^{\circ}\text{K}$  and about  $145^{\circ}\text{K}$ , from where  $T_2$  increases gradually with increasing temperature until the melting point is attained. A high temperature plateau region of  $T_2$  was not achieved in our experiments. Our  $T_2$  results differ somewhat from the line width measurements obtained previously for TMS.<sup>3</sup> According to Smith<sup>7</sup>  $\beta$ -TMS exhibits resonance line narrowing in the temperature interval  $135\text{-}160^{\circ}\text{K}$ , and above  $160^{\circ}\text{K}$  the line width is temperature invariant. This implies that our observed line narrowing region is shifted to higher temperatures with

respect to the previously obtained data. This discrepancy may be accounted for by a difference in purity of the samples used in the two studies. Our free induction decay following a  $90^\circ$  pulse showed only a simple decay corresponding to a wide line, whereas the continuous wave experiment<sup>3</sup> revealed a narrow component in addition to the broad line. This narrow component was assigned by Smith<sup>3</sup> to the presence of mobile impurities in the TMS samples. Since we have used a high purity NMR grade sample and no dual line character or other impurity effects (as reported in reference 3) were noticed in our experiments, we believe that our TMS specimens were purer than those employed in the broad line study.<sup>3</sup> A shift of a line width narrowing region towards lower temperatures due to imperfections or/and impurities was observed previously<sup>7</sup> in  $^{19}\text{F}$  broad line studies of potassium and rubidium hexafluorophosphate ( $\text{KPF}_6$  and  $\text{RbPF}_6$ , respectively).

Although the continuous wave line width data of TMS<sup>3</sup> was affected by the presence of impurities, the qualitative analysis of the line width and second moment results does not seem to be influenced by the impurities. Methyl group motion occurs at temperatures well below 77°K and persists in the entire temperature region of study, while the increase in  $T_2$ , or, decrease in line width, is associated with the onset of overall molecular tumbling. Our spin-lattice relaxation data are shown to be consistent with these second moment and line width data.

#### Correlation Effects and Tumbling

The static frame spin-lattice relaxation at the higher temperatures, 174°K to 140°K, is exponential. Below the latter temperature region, deviations from exponentiality increase progressively down to about 108°K, and persist in the remaining temperature region of the high frequency arm ( $\omega_0\tau_c \ll 1$ ) of the  $T_1$  curve. At 77°K, apparently the limit of the low

frequency arm of the  $T_1$  plot, the longitudinal relaxation is only slightly nonexponential. This relaxation behavior is demonstrated in Fig. 1, where three typical plots of  $\log(M_0 - M_z/M_0)$ , the magnetization recovery rate, versus the time,  $t$ , obtained using the  $90^\circ-\tau-90^\circ$  pulse sequence, are given for  $153^\circ\text{K}$ ,  $91^\circ\text{K}$  and  $77^\circ\text{K}$ .  $M_0$  and  $M_z$  are the nuclear magnetizations at thermal equilibrium and at time  $t$  after a  $90^\circ$  pulse, respectively. An exact study of the rotating frame spin-lattice relaxation exponentiality has not been carried out in the present work.

The observed nonexponential behavior of the longitudinal relaxation in the TMS  $\beta$  phase below  $140^\circ\text{K}$  is assigned to the fact that the motion of the protons within each methyl group is correlated. Runnels<sup>8</sup> and Hilt and Hubbard<sup>9</sup> predicted nonexponential spin-lattice relaxation for spin  $1/2$  systems where three identical spins at the apexes of an equilateral triangle rotate about the threefold symmetry axis. Baud and Hubbard<sup>10</sup> later confirmed this phenomenon experimentally for solid acetonitrile ( $\text{CH}_3\text{CN}$ ), and have shown that intermolecular interactions tend to reduce<sup>10</sup> the nonexponentiality caused by this correlated motion effect inherent in such three spin sets.

The TMS longitudinal relaxation nonexponentiality variation with temperature below  $108^\circ\text{K}$  qualitatively follows the predictions of the Hilt and Hubbard theory,<sup>9</sup> namely marked deviations from exponential behavior in the region of short correlation times ( $\omega_0\tau_c \ll 1$ ), less severe deviations near the minimum and slight deviations in the long correlation time region ( $\omega_0\tau_c \gg 1$ ). Although the intermethyl dipolar interactions in  $\beta$ -TMS quantitatively reduce the degree of nonexponentiality, the non-exponential magnetization recovery curves and the variations with temperature are clearly evident in Fig. 1.

In light of these observations it is necessary to explain why the relaxation gradually becomes more exponential above about  $108^\circ\text{K}$  and indeed

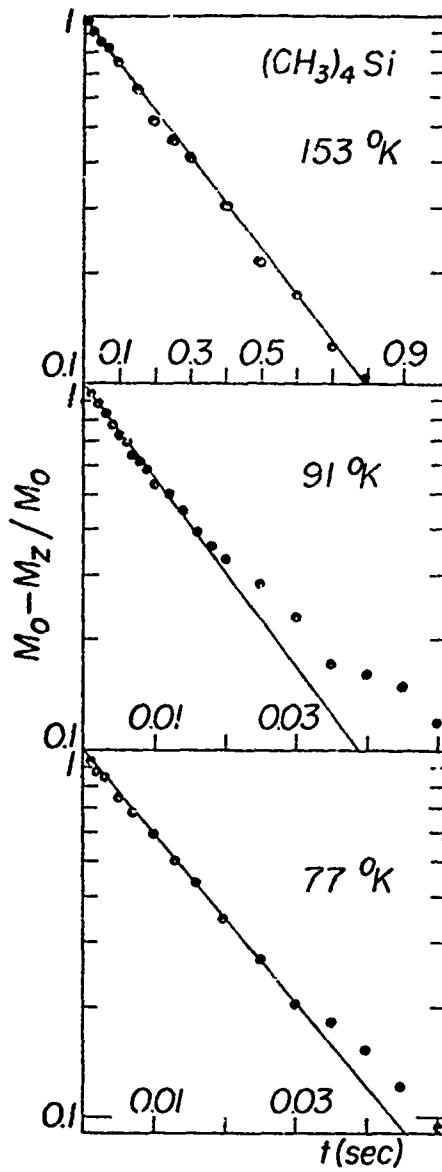


Figure 1: Semilog plots of the magnetization recovery rate,  $M_0 - M_z / M_0$ , versus  $t$  (time) for protons in  $(\text{CH}_3)_4\text{Si}$  at  $153^\circ\text{K}$ ,  $91^\circ\text{K}$  and  $77^\circ\text{K}$  obtained by  $90^\circ - \tau - 90^\circ$  pulse sequence at 25.3 MHz.  $M_0$  and  $M_z$  are the nuclear magnetizations at thermal equilibrium and at time  $t$ , respectively. The spin-lattice relaxation time was derived from the slope of the solid line.

becomes exponential above about 140°K. We suggest that the motion of the molecular frame to which the methyl group is attached reduces the effect of cross-correlations within a methyl group and restores, to some degree, exponential relaxation. Indeed, the longitudinal relaxation becomes exponential near about 140°K when the TMS molecular tumbling characteristic correlation time is about  $2.2 \times 10^{-3}$  sec (see  $T_{1p}$  curve), and remains exponential while the tumbling correlation time becomes progressively shorter up to the TMS melting point. These observations imply that the degree of the relaxation exponentiality for TMS is related to the rate of molecular tumbling, and that even a very slow tumbling rate, as at 118°K where  $\tau_c \sim 0.42$  sec, the relaxation is affected. The fact that methyl group rotation and molecular tumbling have quite different frequencies at any one temperature allows us to resolve between the opposing effects of correlated motions within a methyl group and molecular tumbling.

In view of the TMS results, consideration has to be given to the possibility that the degree of nonexponentiality of the proton longitudinal relaxation in solids containing  $\text{CH}_3$  groups is sensitive to certain molecular reorientations. In support of this proposal there are some additional experimental facts. For protons in the dimethyl aluminum dimer,  $\text{Al}_2(\text{CH}_3)_6$ , only nonexponential longitudinal relaxation was observed,<sup>11</sup> and the proton second moment and spin-lattice relaxation results support the fact that no molecular motion other than methyl rotation about the triad axes takes place.<sup>11</sup> A situation very similar to that for  $(\text{CH}_3)_4\text{Si}$  was found<sup>12</sup> for ammonia in the high frequency arm of proton  $T_1$  plot, namely nonexponential decays at low temperatures with the nonexponentiality decreasing with increasing temperature up to 150°K. The temperature

dependence of the proton line width<sup>12</sup> and  $T_{1p}$  observations for ammonia were interpreted<sup>13</sup> in terms of the onset of self-diffusion near 160°K.

In the tetramethylammonium halides the spin-lattice relaxation of proton decays exponentially in the entire temperature region,<sup>14</sup> and it was also found<sup>15, 14</sup> that besides methyl group rotation, cation tumbling is an effective relaxation process at higher temperatures so that cation tumbling is expected to occur in the entire temperature range of investigation. For this last example, however, the observation of exponential relaxation can also arise due to only the intermolecular interactions. The existence of molecular reorientations is certainly not the only cause for obtaining exponential decays, but seems to be an important factor that should often be considered. It appears that the exponentiality of the relaxation could be used by itself as an indication for the presence of reorientations of the molecules in the type of solid in question, and perhaps gain information on interactions and motions in solids. This phenomenon has to be investigated further in the future.

#### Model and Motions

Since the log of the magnetization recovery rate vs. time, in the non-exponential relaxation region for  $\beta$ -TMS, exhibits a clear, straight line for short  $t$  values and the deviations from exponentiality are relatively small, the spin-lattice relaxation time was derived systematically from the slope of the initial straight line portion of the decays in question as demonstrated in Fig. 1. The obtained proton  $T_1$  and  $T_{1p}$  vs. the inverse temperature are shown in Fig. 2 as semilog plots.  $T_1$  decreases with the temperature down to about 90°K, where a minimum in the  $T_1$  curve is obtained.

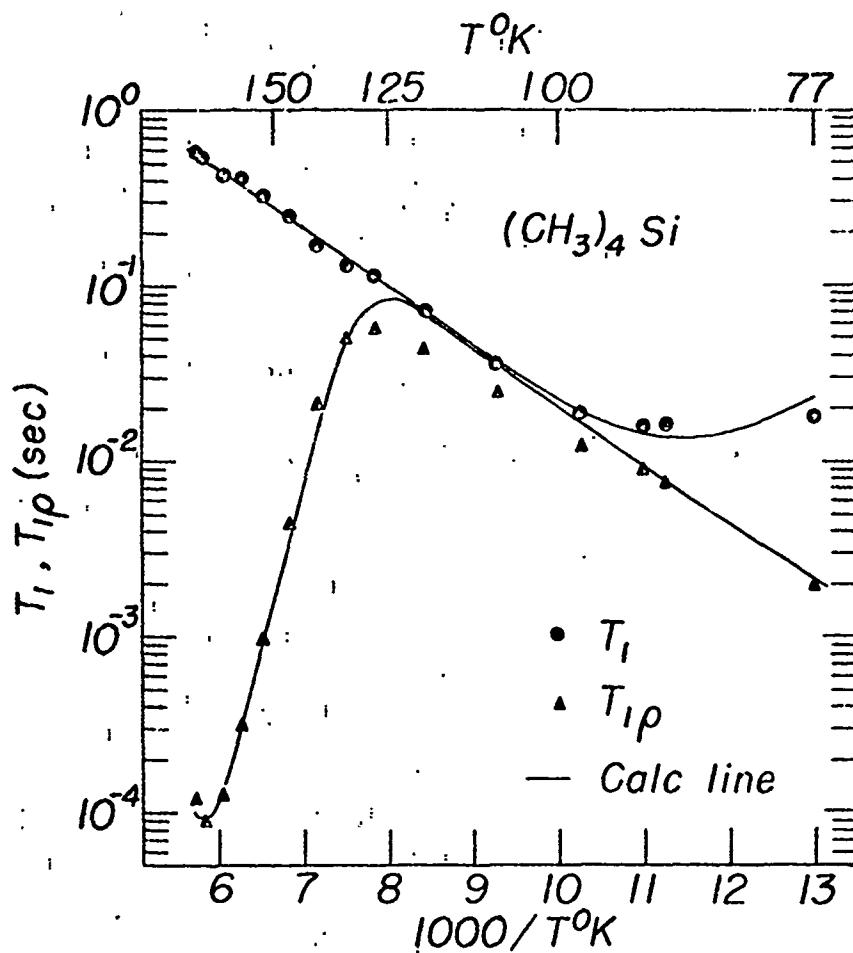


Figure 2: The temperature dependence of the proton spin-lattice relaxation time in the static and rotating frame ( $T_1$  and  $T_{1\rho}$ , respectively) for solid  $(CH_3)_4 Si$  obtained at 25.3 MHz. The solid line was calculated using equations (1) and (2) and employing the parameters given in Table I.

$T_{1p}$  reaches its highest value at about  $127^{\circ}\text{K}$ . Below this temperature  $T_{1p}$  decreases with the temperature and has the same slope as the  $T_1$  curve. Above  $127^{\circ}\text{K}$   $T_{1p}$  decreases with increasing temperature and a minimum is attained at  $171^{\circ}\text{K}$ . We associate the  $T_1$  curve and the part of the  $T_{1p}$  plot below  $127^{\circ}\text{K}$  with a rotation of the methyl group about its triad axis. The V shaped part of  $T_{1p}$  plot corresponds to the overall molecular tumbling of the TMS molecules.

The fluctuations in the dipolar interaction due to these two motions are the dominant relaxation mechanisms in TMS. However the analysis of this composite motion has to take into account that the methyl group rotation and the overall tumbling of the molecule which contains the methyl groups do not produce independent spin-lattice relaxation contributions.<sup>16, 17</sup> Neglecting intermethyl group interactions and employing a similar analysis to that used for the tetramethylammonium halides<sup>14</sup>  $T_1$  and  $T_{1p}$  (in the weak collision limit) are given as follows:

$$1/T_1 = (3/20)(\gamma_H^4 \hbar^2 / r^6) [g(\omega_0, \tau_{c1}) + 3g(\omega_0, \tau_{c2})] \quad (1)$$

$$1/T_{1p} = (3/20)(\gamma_H^4 \hbar^2 / r^6) [g_p(\omega_0, \tau_{c1}, \omega_1) + 3g_p(\omega_0, \tau_{c2}, \omega_1)] \quad (2)$$

where

$$g(\omega_0, \tau_c) = \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \quad (3)$$

$$g_p(\omega_0, \tau_c, \omega_1) = \frac{5}{2} \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{\tau_c}{1 + 4\omega_0^2 \tau_c^2} + \frac{3}{2} \frac{\tau_c}{1 + 4\omega_1^2 \tau_c^2} \quad (4)$$

and

$$\tau_{c2}^{-1} \equiv \tau_c^{-1} + \tau_{c1}^{-1} \quad (5)$$

Here,  $\tau_c$  is the correlation time for methyl group rotation,  $\tau_{c1}$  the correlation time for overall molecular tumbling,  $\omega_0$  the resonance frequency,  $\omega_1 \equiv \gamma_H H_1$ ,  $r$  is the interproton distance within a methyl group and the

other symbols have their usual meaning. Since the methyl group rotation and the tumbling motion take place with widely separated frequencies at any temperature, we can assume that near the minimum in the  $T_1$  curve the correlation time for tumbling is very long, namely  $\tau_{c1} \rightarrow \infty$ . Thus equation (1) reduces to the normal  $T_1$  expression for methyl group rotation:<sup>18</sup>

$$1/T_1 = (9/20)(\gamma_H^4 \hbar^2 / r^6) g(\omega_0, \tau_c) . \quad (6)$$

On the other hand, near the minimum of the  $T_{1\rho}$  curve methyl group rotation is very fast, and tumbling becomes the effective relaxation mechanism.

Equation (2) then reduces to:

$$1/T_{1\rho} = (3/20)(\gamma_H^4 \hbar^2 / r^6) g_\rho(\omega_0, \tau_{c1}, \omega_1) . \quad (7)$$

Minimum values for the  $T_1$  and  $T_{1\rho}$  expressions in equations (6) and (7) are obtained when  $\omega_0 \tau_c \approx 0.616$  and  $\omega_1 \tau_c \approx 0.5$ , respectively. Taking for the proton-proton distance within a methyl group in  $\beta$ -TMS a value of  $1.79 \text{ \AA}^0$  and utilizing a  $H_1$  value of 3.3 gauss, we are able to calculate values for the  $T_1$  and  $T_{1\rho}$  minima and these are tabulated in Table I. These calculated minimum values are in agreement with the corresponding experimental results, also shown in Table I. Tumbling and methyl group rotation are assumed to be activated processes, and accordingly we describe the variation in motional rate and temperature by

$$\tau_c = \tau_{o1} \exp(E_a/RT) \quad \tau_{c1} = \tau_{o1} \exp(E_{a1}/RT) \quad (8)$$

where  $E_a$ ,  $E_{a1}$  and  $\tau_{o1}$ ,  $\tau_{o1}$  are the activation energies and the inverse frequency factors for methyl and tumbling motions, respectively. The activation energies for methyl group rotation and the molecular tumbling motion have been calculated from the straight line portion slopes of the high temperature arm in the  $\log T_1$  vs.  $T^{-1}$  plot and from the low temperature

arm in the  $\log T_{1\rho}$  vs.  $T^{-1}$  curve, respectively, using equations (6), (7) and (8). The corresponding  $T_o$ ,  $T_{o1}$  values have been obtained from the temperatures of the appropriate minimum values employing equations (8). The  $E_a$ ,  $E_{a1}$  and  $T_o$ ,  $T_{o1}$  values are given in Table I. On substituting the latter parameters into equations (1), (2) and (8) the solid lines shown in Fig. 2 were obtained, and generally speaking these fit our experimental results.

Considering that our calculated  $T_1$  and  $T_{1\rho}$  data are based only on intramethyl group relaxation contributions, we would expect the calculated  $T_1$  and  $T_{1\rho}$  values to be systematically higher than the observed values. However, we did find agreement between the calculated and observed  $T_1$  and  $T_{1\rho}$  values. The  $T_1$  agreement may be understood if we remember that intramethyl group cross-correlation effects will tend to retard relaxation and give longer relaxation times than one normally would expect. The  $T_{1\rho}$  agreement indicates that the reorientations of the TMS molecules are not entirely random, and that there is some degree of correlation between the motion of the molecules.<sup>10, 19</sup> Such correlation effects displace the  $T_1$  and  $T_{1\rho}$  curve to higher values. In TMS this shift appears to be nearly equal to intermethyl relaxation contribution, and these two opposing effects compensate each other causing  $T_1$  and  $T_{1\rho}$  to be nearly equal to the intramethyl group dipolar interactions. The presence of correlation between the reorientations of the TMS molecules is supported by the relatively short inverse frequency factor of  $4.5(\pm 0.3) \times 10^{-17}$  sec determined for the molecular tumbling motion. Such a small pre-exponential factor of  $10^{-18}$  sec was obtained by Blinc<sup>20</sup> for proton jumps in  $KH_2PO_4$  and was assigned to a high correlation in the proton jumps.

Between  $127^0K$  and  $90^0K$  some disagreement between the calculated and experimental  $T_{1\rho}$  data can be observed in Fig. 2. Such discrepancies have been reported previously<sup>4, 21</sup> and as yet have not been explained. In the

$\beta$  phase of TMS it seems to be affected by possible deviations from exponentiality in  $T_{1p}$  in the temperature interval in question. Better agreement between the calculated and experimental  $T_{1p}$  values is obtained below 90°K, where deviations from nonexponentiality are reduced.

Deviations between the calculated and observed  $T_1$  data appear in the vicinity of the observed  $T_1$  minimum near ~90°K as well as below this temperature. From the flat and shallow feature of the observed  $T_1$  minimum along with the low activation energy of  $1.57 \pm 0.08$  kcal/mole associated with this  $\text{CH}_3$  rotation it is reasonable to expect that to some degree the  $\text{CH}_3$  relaxation mechanism is governed by quantum mechanical tunneling effects.<sup>22</sup> The low temperature NMR proton spectrum as well as relaxation studies below 77°K may elucidate these possibilities.

The methyl group activation energy we have determined for TMS is consistent with the trend shown in reference 3 for the  $\text{CH}_3$  motions in the group IV tetramethyl compounds, namely that the  $\text{CH}_3$  rotational barrier decreases on going from  $(\text{CH}_3)_4\text{C}$  to  $(\text{CH}_3)_4\text{Pb}$ . The order of magnitude of the  $T_0$  values for all the tetramethyl compounds in question is  $10^{-12}$  sec. The  $\text{CH}_3$  torsional barriers for  $(\text{CH}_3)_4\text{Z}$  when Z = C, Si, Ge and Sn have been calculated recently<sup>23</sup> from far infra-red spectra and reveal the same trend as the NMR results. However, these infrared barriers<sup>23</sup> are systematically higher than the corresponding NMR values. The potential barrier shape assumptions used to derive the infrared barrier heights are a probable source for this disagreement; such approximations have not been made in analyzing the NMR data. For  $\beta$ -TMS the far infrared results yield a  $\text{CH}_3$  barrier of 2.0 kcal/mole in comparison with a value of  $1.57 \pm 0.08$  kcal/mole obtained in the present study. A value of  $1.3 \pm 0.2$  kcal/mole was determined from calorimetric studies<sup>5</sup> for this barrier, and is in very good agreement with our results.

The barrier for tumbling derived from our  $T_{1/2}$  data is higher by about 20% than Smith's value<sup>3</sup> obtained from line narrowing data.<sup>1</sup> Mobile impurities which affected the broad line experiments apparently are able to give a lower activation energy.

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**Table I:** Activation energies,  $E_a$ , inverse frequency factors,  $\tau_o$ , and spin-lattice relaxation minima,  $(T_1)_{min}$ ,  $(T_1_p)_{min}$ , for methyl group and tumbling motions for  $\beta-(CH_3)_3Si$ .

Parameter	Units	Origin	Methyl group rotation	Molecular tumbling
$E_a$	kCal/mole	exp	$1.57 \pm 0.08$	$8.7 \pm 0.5$
$\tau_o$	sec	exp	$4.5(\pm 0.3) \times 10^{-13}$	$4.5(\pm 0.3) \times 10^{-17}$
$T_1(min)$	sec	exp	$1.55(\pm 0.08) \times 10^{-2}$	---
$T_1(min)$	sec	calc	$1.43 \times 10^{-2}$	---
$T_1_p(min)$	sec	exp	---	$8.8(\pm 0.4) \times 10^{-5}$
$T_1_p(min)$	sec	calc	---	$9 \times 10^{-5}$

### Figure Captions

**Figure 1:** Semilog plots of the magnetization recovery rate,  $M_0 - M_z / M_0$ , versus  $t$  (time) for protons in  $(\text{CH}_3)_4\text{Si}$  at  $153^\circ\text{K}$ ,  $91^\circ\text{K}$  and  $77^\circ\text{K}$  obtained by  $90^\circ-\tau-90^\circ$  pulse sequence at 25.3 MHz.  $M_0$  and  $M_z$  are the nuclear magnetizations at thermal equilibrium and at time  $t$ , respectively. The spin-lattice relaxation time was derived from the slope of the solid line.

**Figure 2:** The temperature dependence of the proton spin-lattice relaxation time in the static and rotating frame ( $T_1$  and  $T_{1\rho}$ , respectively) for solid  $(\text{CH}_3)_4\text{Si}$  obtained at 25.3 MHz. The solid line was calculated using equations (1) and (2) and employing the parameters given in Table I.

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13. Abstract:

The  $\beta$  phase of high purity samples (99.9% min) of tetramethylsilane (TMS),  $(\text{CH}_3)_4\text{Si}$ , was investigated between 77°K and its melting point (174°K) employing static and rotating frame proton spin-lattice relaxation ( $T_1$  and  $T_{1\rho}$ , respectively) measurements. Minima in the  $T_1$  curve near 90°K and in  $T_{1\rho}$  at 171°K correspond to methyl group reorientation and overall molecular tumbling, respectively. Activation energies and inverse frequency factors for both motions are derived and discussed. Deviations from exponential behavior in the longitudinal relaxation were noted below 140°K and are inferred to be due to a correlation in the relative motion of the protons within each methyl group. The exponentiality of the spin-lattice relaxation above ~140°K is associated with the onset of overall molecular tumbling motions. It is suggested that the presence of exponential proton magnetization decays in solids containing methyl groups may sometimes serve as an indication for the presence of reorientations of the molecular frame to which the methyl groups are attached. The possibility that the existence of exponential and nonexponential decays may be used by itself to gain information on interactions and motions in solids, has to be further investigated.